Renewable and Sustainable Energy Reviews 14 (2010) 2580–2595

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Exergy based performance evaluation of latent heat thermal storage system: A review

S. Jegadheeswaran [a,*], S.D. Pohekar [a], T. Kousksou [b]

[a] *Mechanical Engineering Area, Tolani Maritime Institute, Induri, Talegaon-Chakan Road, Pune 410 507, India*
[b] *Laboratoire de Thermique Énergétique et Procédés, Avenue de l'Université, BP 1155, 64013 Pau Cedex, France*

ARTICLE INFO

Article history:
Received 20 May 2010
Accepted 19 July 2010

Keywords:
Latent heat thermal energy storage
Exergy analysis
Entropy generation
Thermoeconomics

ABSTRACT

Phase change material (PCM) based latent heat thermal storage (LHTS) systems provide an attractive solution to bridge the gap between energy source and demand, if source is intermittent and time dependent. The optimization of LHTS systems is not necessarily on the basis of performance study through energy analysis, but on the basis of exergy based performance study. The exergy based performance evaluation and subsequent optimization of LHTS units have been a growing interest among the researchers in recent years. This can be seen through the various works reported in the literature. This paper reviews the various procedures adopted for the exergy based performance evaluation of LHTS units. The influence of operating and design parameters on the exergy stored/retrieved and thus, on the optimization is addressed as a main aspect. The need of exergy analysis for the comparative evaluation of LHTS systems with performance enhancement techniques is emphasized. Thermoeconomics methods applicable to LHTS systems are also presented in this paper.

Contents

1. Introduction . . . 2580
2. Energy analysis of LHTS systems . . . 2581
3. Second law analysis-Thermodynamic concepts . . . 2583
   3.1. Exergy . . . 2583
   3.2. Entropy . . . 2583
   3.3. Second law efficiency . . . 2583
4. Exergy analysis of LHTS systems. . . . 2584
   4.1. Exergy efficiency . . . 2584
   4.2. Exergy evaluation . . . 2585
   4.3. Entropy generation . . . 2586
5. Exergy based optimization of LHTS systems . . . 2588
   5.1. Influence of HTF . . . 2589
   5.2. Influence of PCM . . . 2589
   5.3. Influence of system dimensions . . . 2590
6. Exergy analysis with performance enhancement techniques . . . 2591
   6.1. Multiple PCMs method . . . 2591
   6.2. Addition of fins, thermal conductivity enhancement and microencapsulation of PCM . . . 2592
7. Thermoeconomic analysis . . . 2593
8. Conclusions . . . 2593
   References . . . 2594

1. Introduction

The large scale utilization of the many sources of thermal energy like solar thermal energy, hot waste streams available in industries, etc., may be handicapped, if not properly managed. The

* Corresponding author. Tel.: +91 2114 242044; fax: +91 2114 241517.
E-mail address: jdees.2002@gmail.com (S. Jegadheeswaran).

1364-0321/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.rser.2010.07.051

Nomenclature

c	specific heat (J/kg K)
Ex	exergy (J)
$\dot{E}x$	exergy rate (W)
f	liquid fraction
h	specific enthalpy (J/kg)
L	latent heat (J/kg)
M	mass of PCM (kg)
$\dot{m}$	mass flow rate of HTF (kg/s)
N_s	entropy generation number
NTU	number of transfer units
P	pressure (Pa)
Q	instantaneous heat transfer rate (W)
R	ideal gas constant (J/kg K)
S	entropy (J/K)
T	temperature (°C or K)
T_m	melting temperature (°C or K)
t	time (s)
V	volume (m^3)
Greek symbols	
ρ	density (kg/m^3)
η	energy efficiency
ψ	exergy efficiency
Subscripts	
char	charging
dis	discharging
final	final condition
gain	gained amount
HTF	heat transfer fluid
in	inlet
init	initial condition
l	liquid phase
loss	lost amount
o	environment
out	outlet
PCM	phase change material
s	solid phase
stored	stored amount
wall	heat exchanger wall

major problem in managing energy from the above-mentioned sources is the time gap between the availability and the need. Employment of effective energy storage/retrieval device is emphasized, if the energy source is intermittent and time dependent. For the last three decades, there has been a growing interest in latent heat thermal storage (LHTS) technique, which is proved as a better engineering option over sensible heat storage. The relative merits of LHTS include large energy storage for a given volume, uniform energy storage/supply, compactness, etc.

In LHTS units, phase change materials (PCM) are employed, which undergo change of phase (solid to liquid and vice versa) during the energy transfer process. In addition to the above stated advantages, extensive studies on wide range of PCMs, have made LHTS unit as a potential system in various engineering fields. For comprehensive details of various PCMs and their applications, readers are referred to the recent review articles by Farid et al. [1], Sharma and Sagara [2], Zalba et al. [3] and Kenisarin and Mahkamoy [4].

However, the employment of LHTS units for energy storage/retrieval can be realized only if the performance of the unit is known. The performance assessment of any LHTS unit requires a thorough knowledge about the thermal behavior of PCM that is employed. Accordingly, a great amount of work both numerically and experimentally has been devoted on the study of thermal behavior of different configurations of LHTS units applicable to various fields. Some of the works are also extended to investigate the influence of various geometric, operating and design parameters on the thermal behavior. Investigations by Trp [5] (shell and tube LHTS for solar thermal applications), Regin et al. [6] (LHTS loaded with cylindrical capsule PCM for solar water heater), Zukowski [7] (LHTS with encapsulated PCM for solar space heating), Chen et al. [8] (PCM packed in a box-type solar cooker), Akgun et al. [9] (PCM packed in a conical shell and tube LHTS) and Guo and Zhang [10] (Aluminium foil attached LHTS for solar power generation) are some notable works in recent years focusing on the above-mentioned points.

Once the thermal behavior is known, the performance of LHTS units can be evaluated through two approaches. They are:

- By applying energy conservation principle (based on first law of thermodynamics).
- By applying exergy principle (based on second law of thermodynamics).

The effective handling of performance evaluation of LHTS unit would result in optimized system for the application of interest.

However, in a recent review, Verma et al. [11] have stressed the need for exergy analysis for LHTS units. Based on this, it is felt that the exergy analysis should be taken as a main aspect in the future research works on LHTS units. This paper is motivated from the above point and is intended to review the works on various exergy based performance evaluation techniques employed for LHTS units. This review is intended to provide necessary guidelines for the future exergy based studies.

2. Energy analysis of LHTS systems

The performance of a thermal system can be evaluated through a well known parameter, efficiency or effectiveness. As far as LHTS systems are concerned, the efficiency is nothing but a measure of how effectively the heat or cold energy is stored or recovered. In other words, it indicates how much heat or cold that could not be stored or recovered. Hence, the efficiency of LHTS can be determined as charging efficiency or discharge efficiency or overall (complete cycle) efficiency. The terms 'charging' and 'discharging' are used, respectively, for melting and solidification processes of PCM. This is because the heat energy is stored in the PCM during melting and the same is retrieved from the PCM during solidification. However, when it comes to application like air conditioning systems, the desired form of energy is 'cold' which implies that the cold energy is stored during solidification and it is retrieved during melting. In this case 'charging' and 'discharging' can be applied to solidification and melting, respectively. In view of generalization and to avoid confusion, however, we adopt 'charging' for melting (corresponds to heat gained or cold released by PCM) and 'discharging' for solidification (corresponds to heat released or cold gained by PCM).

Many investigators carried out calculation of efficiency or a similar parameter of LHTS units employed for different applications. These investigations have focused on either charging and discharging processes separately or the complete working cycle of the system depending on the application. A system is always expected to produce the maximum possible efficiency, but the system with maximum efficiency is possible only at certain

conditions. Hence, the influence of various design and operating parameters on the efficiency has also been addressed.

El Qarnia [12] calculated the storage efficiency of LHTS used for solar water heater. The efficiency is expressed as a ratio between the latent heat stored in the PCM and the total solar radiation. Higher mass flow rates of heat transfer fluid (HTF) and more number of tubes used in the heat exchanger resulted in maximum storage efficiency. In the similar way, Kaygusuz [13] has computed the storage efficiency of LHTS unit of a solar heat pump. It is reported that stored heat and storage efficiency of LHTS were found to be increasing with increase in mass flow rate of HTF. In addition to that, the effect of inlet temperature of HTF on the storage capacity was studied and the effect is reported as less significant.

Seeniraj et al. [14] investigated the thermal performance of shell and tube LHTS unit employed for space based power generation. The thermal performance was studied using a quantity which is the ratio between the total heat stored and the maximum latent heat that can be stored. The results have once again proved that higher mass flow rates of HTF would lead to high storage performance. Moreover, it is shown that the storage performance is higher in case of smaller size unit as compared to that of larger one.

Although Canbazoglu et al. [15] have not calculated the efficiency, the total heat (sensible + latent heat) that can be stored in the PCM was calculated to compare the storage capacity of various hydrated salts. The LHTS unit taken up for the study is the one integrated with solar water heaters.

In some applications, the performance of LHTS system must be known during discharging period rather than during charging period. Gumus [16] has designed a LHTS unit for preheating of internal combustion engines at cold conditions. Hence, the efficiency was calculated during discharging process which is expressed as ratio of energy gained by engine components and total heat stored in the unit. It is found that the discharge efficiency of the unit increases with time and the unit could produce a maximum efficiency of 57.5%, which is obviously at the end of the discharging process.

Devahastin and Pitakusuriyarat [17] proposed a shell and tube LHTS unit for drying food products like sweet potato. In this case, performance during the heat recovery process by the HTF is obviously more important. Hence, the authors calculated the rate of extractable energy from the unit using the temperature difference between the inlet and outlet of the HTF. It is also reported that the extractable energy per unit mass flow rate of HTF decreases as the velocity of HTF increases. The rate of heat recovered from the unit is taken as a performance parameter also by Mettawee and Assassa [18]. The heat recovered was calculated from the heat gained by the HTF. The effect of mass flow rate on the heat recovery was found to similar to that reported in the other works.

The calculation of efficiency during both charging and discharging processes but separately can also be found in some works. Kaizawa et al. [19] have used heat storage ratio and heat release ratio as performance parameters. The heat storage ratio is given as,

$$\frac{\text{Total energy stored in the unit}}{\text{Maximum storage capacity of the unit}}$$

Similarly, the heat release ratio is expressed as,

$$\frac{\text{Total energy released by the unit}}{\text{Maximum storage capacity of the unit}}$$

The heat stored and released are calculated from the heat absorbed and released, respectively, by the HTF. The maximum heat storage capacity takes into account the sensible and latent heat capacity of the PCM. The results show that both the performance ratios increase with increase of mass flow rate of HTF at all times.

Mawire and McPherson [20] have defined charging and discharge efficiencies separately for a LHTS unit proposed for solar cookers as follows:

$$\eta_{char} = \left[\frac{\text{Total energy stored in the unit}}{\text{Total energy supplied by the HTF}}\right],$$
$$\eta_{dis} = \left[\frac{\text{Total energy absorbed by the HTF}}{\text{Total energy stored in the unit}}\right]$$

However, the results of these efficiencies are not reported, as the objective of the work was limited to development of control techniques for control problems.

The complete cycle or overall efficiency of the system has also been used by some researchers. Mettawee and Assassa [21] have defined mean daily efficiency for a LHTS integrated with a solar collector which is used for hot water production. The mean daily efficiency considers total heat absorbed by HTF and total incoming radiation as output and input, respectively. Exactly in the similar way, Sharma et al. [22] have calculated a performance parameter to represent the overall performance of a LHTS of solar cooker. However, the effect of operating/design parameters on the efficiency is not discussed in these papers.

From the summary given above, one may think that detailed information on system efficiency or capacity either during charging and discharging separately or during the complete working cycle along with the influence of various operating/design parameters are explored. Subsequently, the explored information would enable the designer to develop an optimum system. However, the performance of LHTS units is assessed using only energy balance in these studies. This procedure, in fact, is based on first law of thermodynamics and generally employed to identify the ways to improve the quantity of heat stored/recovered. At this point, it is important to mention the popular quote by Bejan [23] which is

> *"the primary purpose of a thermal energy storage system is not, as the name implies, to store the energy, rather, to store useful work".*

From this perspective, it can be stated that first law based analysis, i.e. energy analysis becomes inadequate as information on usefulness of energy cannot be obtained. In other words, energy analysis does not reflect the quality of energy stored/recovered. Hence, an 'optimized LHTS unit' based on energy analysis is not necessarily an optimum system. This inadequacy can be overcome, if an analysis based on second law of thermodynamics is carried out for LHTS units. This is because the degradation of energy stored/recovered is very much appreciated only in the second law analysis. Rosen et al. [24] have reported that energy analysis is complicated and confusing when it comes to cold thermal storage systems those correspond to one employed for building cooling. This is because only heat flows are taken into account rather than cold flows, in energy analysis. On the other hand, second law based analysis can treat both heat and cold which is out of equilibrium with the environment, as a valuable commodity. Hence, second law analysis is inherently the better option than energy analysis especially in case of cold thermal storage systems. Moreover, a thermoecomomics analysis of a thermal system is necessarily based on second law analysis in order to obtain feasible design and operating conditions. This is because only second law analysis correctly reflects the economic value of the storage operation [25]. Thermoeconomics analysis combines second law analysis and

Table 1
Benefits of second law analysis in LHTS systems.

S No	Benefits
1	Quality of energy stored/recovered can be measured
2	Destroyed energy quality as well as lost energy quality can be quantified
3	Causes of internal and external irreversibilities can be identified
4	Both heat and cold can be treated as valuable commodities
5	Provides a meaningful base for themoeconomics analysis

engineering economics. Since the second law analysis takes into account the true potential of energy, estimation of cost and subsequent optimization of the system can be realized through thermoeconomics. Further discussion on thermoeconomics analysis of LHTS systems is presented in the final section of this paper. The benefits of second law analysis are highlighted in Table 1.

3. Second law analysis-Thermodynamic concepts

The second law of thermodynamics is very distinct from the first law as it introduces new concepts of exergy and entropy. Hence, the analysis based on the second law of thermodynamics needs to be established with a clear understanding of these concepts. This section overviews the concepts of exergy and entropy and their roles in the second law based analysis.

3.1. Exergy

Unlike first law of thermodynamics, second law of thermodynamics quantifies the quality of energy. The quality of energy is gauged from the state of system in relation to the surrounding conditions. This quality or usefulness of energy is termed as "exergy". Many more equivalent terms like availability, available energy, essergy, work capability, utilizable energy, etc., can be found in literature. However, Kaygusuz and Ayhan [26] have reported that use of the term exergy should be encouraged, as it was agreed at the *"Fourth International Symposium on Second Law Analysis of Thermal System"* held at Rome, Italy in 1987. Moreover, the term exergy is more commonly employed than others. Hence, in this paper, we are confined to the term exergy. Since second law of thermodynamics introduces "exergy", the analysis based on second law is widely called exergy analysis.

Exergy is defined as maximum quantity of work that can be produced by a system as it comes to equilibrium with surrounding. In other words, exergy is nothing but a measure of potential of the system to cause change, due to its non-equilibrium condition with surrounding. A system can carry exergy only if it is not in equilibrium with surrounding and the exergy becomes more and more as the system deviates more and more from surrounding. Once the equilibrium is attained then exergy becomes zero. This means exergy cannot be conserved, but can be consumed or destroyed. This statement highlights the reason why energy is getting degraded.

It is clear from the abovementioned points that the degradation of energy is automatically accounted for in the analysis, if it is second law (exergy) based analysis. As mentioned earlier, the LHTS system is for storing useful work. Also the recovery of useful work is equally important. Hence, the calculation of exergy transfer is more appropriate than the calculation of energy transfer during charging and discharging processes. Since a LHTS unit is concerned with only heat transfer, the exergy depends on the temperature at which it is available in relation to the temperature of surrounding.

3.2. Entropy

The exergy content of a system or a matter can be obtained using the thermodynamic relations known as entropy relations. As the name implies, these relations are basically expressed for a property known as entropy. The association between entropy and second law of thermodynamics is well known as the latter is often called law of entropy.

Moreover, as we have seen before, unlike energy, exergy cannot be conserved, rather is destroyed. However, exergy can be conserved, if the process takes place in a reversible manner. It is well known that all real processes are irreversible and hence, the irreversibilities associated with the process can be stated as responsible for the exergy destruction. The exergy analysis is not only concerned with exergy, but also with exergy destruction. This means that it is also necessary to know that to what extent exergy can be destroyed in order to quantify the true potential of the system/process. This is where the concept of entropy becomes more useful.

Entropy here is used as a measure of irreversibility. This is explained as follows. Any process which is irreversible, is accompanied by energy degradation and when the equilibrium is attained, the exergy content reaches zero value. At the same time, the irreversible process is also accompanied by increase in entropy which reaches a maximum when the system comes in equilibrium with surrounding. Thus, all irreversible processes proceed in the direction of increase in entropy and decrease in exergy. This highlights the relation between exergy and entropy. In actual system, entropy is always generated and exergy is destroyed. Hence, the destroyed exergy must be proportional to generated entropy. As standard entropy relations are much easier to deal with, the generated entropy is included in the exergy analysis to explore the destroyed exergy quantity. The generated entropy is expressed in terms of entropy generation number which will be discussed further in the subsequent sections.

3.3. Second law efficiency

First law based efficiency can be stated as the ratio of energy output and energy input. In practical thermal systems the energy output is less than energy input because of energy loss. The first law efficiency indicates the amount of loss that occurs during the process in the system. Hence, efficiency can be improved only by reducing losses. However, the losses do not reflect the degradation of energy. To LHTS units, this is of more important, which can be explained as follows:

The efficiency of a well insulated LHTS unit during the cycle (comprises of melting and solidification processes) can be defined as the ratio between total energy recovered during solidification and total energy stored during melting. Since the latent heats of both melting and solidification are the same, the efficiency of the LHTS unit becomes 100%. Due to the adiabatic condition, no energy loss can occur. Nevertheless, energy would be destroyed due to internal irrerversibilities. Even if the realistic condition of non-adiabatic is included in the analysis, the energy efficiency cannot reflect the destroyed quantity as it measures only energy loss due to infiltration. On the other hand, the second law or exergy efficiency which takes into account the exergy, can identify and quantify both the destroyed quantity as well as lost quantity. Due to this reason, the exergy efficiency is found to be less in LHTS systems when compared to energy efficiency [24,27–34]. This can be seen from Table 2 in which the investigations presenting the comparison between energy and exergy efficiency are summarized.

The second law or exergy efficiency of a thermal system is thus, defined as the ratio of exergy output and exergy input. For a given quantity of exergy, the output exergy is less due to exergy destruction. As we know exergy destruction is due to irrerversibilities. Thus, exergy efficiency is a measure of irrerversibilities and is defined as,

Table 2
List of works presenting the comparison between energy and exergy efficiencies.

Ref.	LHTS module	Application	Operation mode	Exergy efficiency based on	Exergy efficiency in comparison with energy efficiency[a]
[24]	Rectangular tank	Cold thermal storage	Cycle	Exergy contents	Less by 80%
[27]	Not available	General	Cycle	Exergy contents	Less by 60%
[28]	Cylindrical tubes	Solar space heating	Cycle	Exergy contents	Less by 37%
[29]	Cylindrical tubes	Solar space heating	Cycle	Exergy contents	Less by 35%
[30]	Cylindrical tank	Solar green house	Charging	Exergy contents	Less by 25%
[31]	Rectangular tank	Solar collector	Charging	Entropy generation	Less by 95%
[32]	Spherical capsules	General	Charging	Entropy generation	Less by 83%
[33]	Shell and tube	General	Discharging	Exergy contents	Less by 47%
[34]	Spherical capsules	Cold thermal storage	Charging and discharging	Entropy generation	Less by 7% (charging); Less by 14% (discharging)

[a] Approximate representative values.

$$\psi = 1 - \left[\frac{\text{Exergy destroyed}}{\text{Exergy input}}\right]$$

As already mentioned, the more exergy is destroyed the more is the generated entropy. Hence, the ratio of destroyed exergy and exergy input can be replaced by a factor called entropy generation number (N_s). This implies that,

$$\psi = 1 - N_s \tag{1}$$

Eq. (1) shows that the system performance can be improved by minimizing the entropy generation number. The entropy minimization is taken as an important criterion in the thermal system optimization [35].

From the above discussions, it is clear that exergy and entropy are closely associated with each other and the analysis based on second law of thermodynamics revolves around these two. For more comprehensive discussion on exergy and entropy, it is suggested to refer to the paper by Dincer and Cengel [36].

4. Exergy analysis of LHTS systems

In general, exergy analysis is based on the thermodynamic concepts associated with second law of thermodynamics along with conservations principles of mass and energy. It is widely proved that exergy analysis is very effective tool or compliment to energy analysis for performance assessment and optimization of thermal systems. This section presents the exergy methodologies, i.e. methods of evaluation of exergy based performance parameters applicable to LHTS systems.

4.1. Exergy efficiency

Rosen [37] has pointed out that though energy based efficiencies for thermal energy storage systems are reasonable and widely applied, more meaningful efficiencies are defined based on exergy.

The exergy efficiency is evaluated by establishing the exergy analysis and subsequently, the system can be optimized in such a way that the exergy efficiency of the system is maximum possible. Similar to energy efficiency, the exergy efficiency is expressed for charging period and discharging period separately or for the complete cycle.

During charging mode, the HTF transfers the exergy to PCM and part of the exergy is stored in the PCM. Hence, the exergy stored is considered as desired output in the definition of exergy efficiency. Accordingly, the exergy efficiency is expressed as given by Watanabe and Kanzawa [38],

$$\psi_{char} = \frac{\text{Exergy stored in the PCM}}{\text{Exergy supplied by the HTF}}$$

Since in LHTS systems the heat transfer is time dependent, it is also important to evaluate the exergy efficiency at different times during melting. This prompts to define the exergy efficiency in terms of exergy rate. So,

$$\psi_{char} = \frac{\text{Rate of exergy stored in the PCM}}{\text{Rate of exergy supplied by the HTF}}$$

However, Rosen and Dincer [39] have reported that the power input to handle the HTF (pump work) must be accounted for in the exergy efficiency evaluation. The authors have demonstrated that the difference between the exergy efficiency which neglects the pump power and that of considering pump work is significant. Moreover, this difference is more pronounced in case of exergy efficiency than in case of energy efficiency. An expression for exergy efficiency considering the pump work can be found in [30] and the same is given below:

$$\psi_{char} = \frac{\text{Rate of exergy stored in the PCM}}{\text{Rate of exergy supplied by the HTF} + \text{Power input to compressor or pump}}$$

In the above expressions, the exergy supplied by HTF is nothing but the change in flow exergy of HTF during heat transfer with PCM. The change in flow exergy can be calculated by using the difference between the inlet and outlet temperatures of HTF along with the environment temperature. Hence, the exergy efficiency indicates the amount of exergy stored from the supplied exergy during the heat transfer. The maximum exergy that can be supplied by the HTF, however, is not considered here and hence, the maximum possible exergy storage capacity of LHTS system cannot be obtained. This deficit can be overcome by evaluating the exergy efficiency as defined by Gong and Majumdar [40] and the same is given as,

$$\psi_{char} = \frac{\text{Rate of exergy stored in the PCM}}{\text{Exergy rate possesed by the HTF before contact with PCM}}$$

Similar expression is also reported by Demirel and Ozturk [41]. It is clear from the expression that this form of exergy efficiency takes into account the temperature at which the exergy is available for storing as it uses the difference between the inlet temperature of HTF and environment temperature rather than the difference between the inlet and outlet temperatures of HTF. Thus, it obviously provides the information on how much maximum exergy that can be stored from the maximum available potential work.

Similar expressions can be obtained also for discharging (solidification) mode. In the discharging mode, the exergy output is the exergy gained by the HTF which is the change of flow exergy of HTF. On the other hand, the exergy input is exergy available with the PCM. Hence, the following expression can be given for the exergy efficiency of the system during the discharging process [38].

$$\psi_{dis} = \frac{\text{Exergy gained by the HTF}}{\text{Initial exergy available with the PCM}}$$

This expression provides the total exergy extracted by the HTF from the maximum available exergy with the PCM.

From the perspective of time dependent operation, the exergy efficiency can be defined as [27,40],

$$\psi_{dis} = \frac{\text{Rate of exergy gained by the HTF}}{\text{Rate of exergy released by the PCM}}$$

One can identify the variation of exergy efficiency with respect to time during discharging process from the above expression.

The operation of thermal energy storage systems is inherently a cycle comprises of energy storage process followed by energy removal process. The analysis may lead to serious errors, if this cyclic nature is not accounted for, i.e. analyzing either charging or discharging alone [42]. Although the author has highlighted this point with reference to sensible heat storage systems, it is felt that the same is applicable to LHTS systems too. This is demonstrated by Bellecci and Conti [43] as they could minimize the errors arising from the latter approach by switching over to the former. The study focused on LHTS integrated solar assisted heat engine, nevertheless the overall exergy efficiency calculation is recommended for all applications involving LHTS units. This can also be justified from the results of Gong and Mujumdar [40]. The authors have proved that analysis considering charging alone underpredicts the exergy efficiency significantly. Hence, the calculation of overall cycle exergy efficiency becomes necessary.

The evaluation of exergy efficiency can readily be done from the exergy efficiencies of charging and discharging processes. The required expression is as follows [27],

$$\psi_{overall} = \psi_{char} \cdot \psi_{dis} \tag{2}$$

Alternatively, the overall efficiency is given as [28,29],

$$\psi_{overall} = \frac{\text{Exergy extracted from the PCM by the HTF during discharging}}{\text{Exergy input to the PCM during charging}}$$

It is evident from the above discussions that the several forms of exergy efficiencies are developed and used by the investigators. The various forms of exergy efficiencies are summarized in Table 3. Nevertheless, the evaluation of overall exergy efficiency is proved to be better approach than limiting to charging or discharging modes alone.

Table 3
Various forms of exergy efficiencies.

Efficiency	Expression	Description	Ref.
Charging (ψ_{char})	1. $\frac{Ex_{stored}}{Ex_{HTF}}$	Presents total exergy stored out of supplied	[38]
	2. $\frac{\dot{E}x_{stored}}{\dot{E}x_{HTF}}$	Presents time-wise variation of exergy efficiency	[26]
	3. $\frac{\dot{E}x_{stored}}{\dot{E}x_{HTF}+Pump\,work}$	Takes into account the pumping power	[30]
	4. $\frac{\dot{E}x_{stored}}{\dot{E}x_{HTF,init}}$	Presents maximum possible exergy stored	[40,41]
Discharging (ψ_{dis})	1. $\frac{Ex_{HTF}}{Ex_{PCM,init}}$	Presents total exergy recovered out of supplied	[38]
	2. $\frac{\dot{E}x_{HTF}}{\dot{E}x_{PCM}}$	Presents maximum possible exergy recovered	[27,40]
Overall ($\psi_{overall}$)	1. $\frac{Ex_{recovered}}{Ex_{supplied}}$	Presents total exergy recovered out of supplied	[27]
	2. $\psi_{char}\ \psi_{dis}$	–	[28,29]
Charging/ discharging/ overall	1. $1 - N_s$	Presents the quantity of exergy destroyed	[52]

4.2. Exergy evaluation

The previous section illustrated that the evaluation of exergy efficiency for LHTS systems requires evaluation of exergy associated with PCM and HTF. This section addresses the issues related to calculation of exergies of LHTS systems. Demirel and Ozturk [41] have employed the following expression for the rate of exergy supplied by HTF during charging period.

$$\dot{E}x_{in\,put} = \dot{m}_{HTF} c_{HTF} \left[(T_{HTF,in} - T_{HTF,out}) - T_o \ln\left(\frac{T_{HTF,in}}{T_{HTF,out}}\right) \right] \tag{3a}$$

Eq. (3a) expresses exergy input as the change in flow exergy of HTF as a result of heat transfer. However, as stated earlier, the exergy input can be the exergy content of HTF. The exergy content of the HTF is the minimum useful energy obtainable as it reaches to the state of environment. Therefore, the rate of exergy input can be expressed as given in Eq. (3b).

$$\dot{E}x_{in\,put} = \dot{m}_{HTF} c_{HTF} \left[(T_{HTF,in} - T_o) - T_o \ln\left(\frac{T_{HTF,in}}{T_o}\right) \right] \tag{3b}$$

As it is known, the total exergy input to the PCM during any time interval can be readily obtained by the time integration of the relevant expressions.

During the charging mode of operation, the exergy stored at any time instant is computed from the instantaneous heat transfer rate. The instantaneous heat transfer rate (Q) can be obtained by establishing the energy balance i.e.

$$\text{Heat gained by PCM} = \text{Heat trasnferred by HTF}$$

Thus,

$$Q = \dot{m}_{HTF} c_{HTF} (T_{HTF,in} - T_{HTF,out}) \tag{4}$$

Now, the rate of exergy stored in PCM is given as,

$$\dot{E}x_{stored} = Q\left[1 - \left(\frac{T_o}{T_{PCM}}\right)\right] \tag{5a}$$

The temperature of the PCM (T_{PCM}) is taken as its melting temperature by Gong and Mujumdar [40], as the PCM is assumed to be at its melting temperature right through the melting process. This means the sensible heat of PCM is neglected. However, Farid and Kanzawa [44] have stated that in practical LHTS systems, the sensible heat contributes considerably to the total heat. This is because the PCM is subjected to sensible heating prior to melting and subcooling after solidification. This indicates that the PCM temperature may be different from its melting point before and after the charging/discharging process. Fig. 1 illustrates the temperature profile of PCM during phase change with sensible heating/cooling. As shown in Fig. 1, the beginning of charging process is at its subcooled solid temperature and the charging is terminated when the PCM reaches a superheated temperature. In this case, the temperature of PCM is computed as the average of initial and final temperatures of PCM [41]. However, this is simply

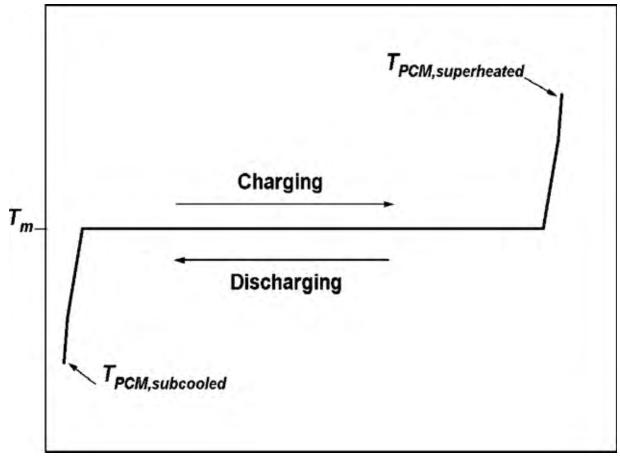

Fig. 1. Temperature profile of PCM during phase change with sensible heating/cooling.

an approximation as its fails to take into account the instantaneous temperatures of PCM. Moreover, at any time, the temperature of PCM is different at different locations because of the continuous movement of solid/liquid interface as the time progresses. Due to this fact, it becomes necessary to consider the temperature variation in the PCM. Hence, it is suggested to evaluate the T_{PCM} as the average of several temperature values measured/calculated at any instant at different locations.

The energy balance used to obtain Eq. (4) assumes that there is no heat loss from the system during the heat transfer, i.e. the system is perfectly insulated. Following this, the exergy balance can be arrived at,

Exergy input = Exergy output + Exergy destroyed

The exergy efficiency based on the above exergy balance can reflect only the destroyed exergy due to internal irreversibilities. According to Erek and Dincer [33], the heat loss/heat gain is the primary parameter in thermal behavior of the system and both the energy and exergy efficiencies depend on the heat loss/heat gain. Moreover, the authors have reported that better agreement could be achieved between numerical and experimental results of energy and exergy analysis when the heat gain was taken into account. From this perspective, the energy balance for charging process may be established as follows in order to include the effect of heat loss/heat gain.

Energy transferred by HTF = Energy gained by PCM
+ Energy lost to the surrounding

Subsequently, the exergy balance is written as,

Exergy associated with HTF = Exergy stored + Exergy destroyed
+ Exergy lost to the surrounding

Hence, the rate of exergy stored is computed from the expression given below:

$$\dot{E}x_{stored} = Q\left[1-\left(\frac{T_o}{T_{PCM}}\right)\right] - Q_{loss}\left[1-\left(\frac{T_o}{T_{PCM}}\right)\right] \tag{5b}$$

where Q_{loss} is the rate of heat loss from the LHTS system due to temperature difference between the system and surrounding.

The total exergy stored in PCM during charging can be readily obtained by performing time integration of Eq. (5b). However, it requires the computation of heat loss to the surrounding. An alternate form, simpler than the time integrated form of Eq. (5b) can be found in Ref. [34] as,

$$\begin{aligned} Ex_{stored} = {} & ML\left[1-\left(\frac{T_o}{T_m}\right)\right] \\ & + Mc_{PCM,s}\left[(T_m - T_{PCM,init}) - T_o \ln\left(\frac{T_m}{T_{PCM,init}}\right)\right] \\ & + Mc_{PCM,l}\left[(T_{PCM,\,final} - T_m) - T_o \ln\left(\frac{T_{PCM,\,final}}{T_m}\right)\right] \end{aligned} \tag{6}$$

The first term on the right hand side of Eq. (6) is the exergy stored during melting and the second and third terms indicate exergy stored during sensible heating before and after the melting, respectively. Eq. (6) is not only simpler but also more direct and appropriate as it also includes exergy stored during sensible heat transfer before and after phase change process.

Similarly, the more appropriate form of exergy balance for discharging process would be,

Exergy of PCM + Exergy gain from surrounding
= Exergy gained by HTF + Exergy destroyed

The exergy balance for a typical LHTS system is illustrated in Fig. 2. Based on exergy balance, the corresponding exergy expressions for discharging process can be obtained in the similar way corresponds to the charging process. The relevant expressions proposed by various investigators are listed in Table 4.

4.3. Entropy generation

The exergy efficiency computed in terms of exergy output and exergy input, for instance, exergy stored in the PCM and exergy supplied by the HTF provides the information on how much exergy is destroyed. Since this class of expressions does not stress the calculation of exergy destruction, one may not be able to identify the reasons for exergy destruction. In other words, since the exergy destruction is due to the internal irreversibilities, no information on when and where the irreversibilities occur, can be obtained. In the process of optimization, however, it is the irreversibilities that

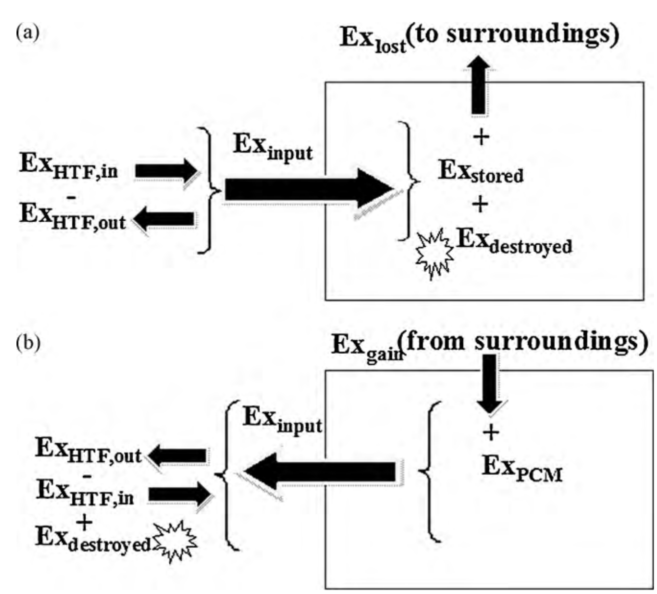

Fig. 2. Exergy balance for a typical LHTS system (a) during charging and (b) during discharging.

Table 4
Expressions of exergy input and output for discharging process.

	Expression	Description	Ref.
Exergy input	1. $\dot{m}_{HTF} c_{HTF} (T_{HTF,out} - T_{HTF,in}) \left[1 - \left(\frac{T_o}{T_{PCM}}\right)\right]$	Presents rate of exergy released by PCM	[27]
	2. $\dot{m}_{HTF} c_{HTF} (T_{HTF,out} - T_{HTF,in}) \left[1 - \left(\frac{T_o}{T_{PCM}}\right)\right] + Q_{gain} \left[1 - \left(\frac{T_o}{T_{PCM}}\right)\right]$	Takes into account the heat gain from surroundings	[33]
	3. $\dot{m}_{HTF} c_{HTF} (T_{PCM} - T_{HTF,in}) \left[1 - \left(\frac{T_o}{T_{PCM}}\right)\right]$	Presents rate of maximum possible exergy released by PCM	[40]
	4. $ML\left[1 - \left(\frac{T_o}{T_m}\right)\right] + Mc_{PCM,s}\left[(T_{PCM,init} - T_m) - T_o \ln\left(\frac{T_{PCM,init}}{T_m}\right)\right] + Mc_{PCM,l}\left[(T_m - T_{PCM,final}) - T_o \ln\left(\frac{T_m}{T_{PCM,final}}\right)\right]$	Presents total exergy released by PCM	[34]
Exergy output	1. $\dot{m}_{HTF} c_{HTF} \left[(T_{HTF,out} - T_{HTF,in}) - T_o \ln\left(\frac{T_{HTF,out}}{T_{HTF,in}}\right)\right]$	Presents rate of exergy recovered by HTF	[27,40]

are to be identified so that an attempt to reduce the same can be made.

The difference between reversible and irreversible process is described quantitatively by the amount of entropy generation. Thus, the entropy generation is the direct measure of internal irreversibility or exergy destroyed. The optimum system can now be developed in which the entropy generation is minimal. In fact Bejan [35] has stated that optimization of a system through entropy generation minimization is distinct from that of through exergy analysis. This is basically because the exergy analysis deals with only thermodynamics where as to calculate and minimize entropy generation one needs to use heat transfer and fluid mechanics principles along with thermodynamics.

For LHTS systems, during charging or discharging process, the net entropy generation (S_{gen}) is written as [32,45–47],

$$S_{gen} = S_{flow} + \Delta S_{PCM} + \Delta S_{HTF} \tag{7a}$$

where S_{flow} is the entropy transfer due to the heat transfer between PCM and HTF. The second and third terms on the right hand side of Eq. (7a) correspond to the entropy variations in the PCM and HTF, respectively.

In the works of Refs. [32,45–47], the PCM was encapsulated in plastic shells and HTF was made flowing through the tank filled with PCM capsules. Hence, the entropy variation of plastic capsules could be neglected. However, other configurations of heat exchangers are also investigated for LHTS units employed for various applications like solar heating systems, A/C systems, waste heat recovery systems, space based solar power systems, etc., For the recent review on various kinds of heat exchangers proposed by researchers, the readers are referred to [48]. Among these shell and tube/concentric double pipe heat exchangers are proved as high efficient for minimum volume [49]. In shell and tube configuration, the wall of the heat exchanger plays a crucial role in the heat transfer as Jegadheeswaran and Pohekar [50] have proved that increasing the wall thickness leads to lesser heat transfer rate. Therefore, the entropy variation of wall needs to be included in the computation of net entropy generation. Accordingly, Erek and Dincer [51] have suggested an expression for entropy variation, which further includes the entropy generation due to the interaction of system with the environment ($S_{heat\ loss/gain}$). Since the authors investigated solidification of PCM, entropy generation due to heat gain by the system from the surroundings is included. The general form of the expression applicable to both charging and discharging processes can be,

$$S_{gen} = S_{flow} + \Delta S_{PCM} + \Delta S_{HTF} + \Delta S_{wall} \pm \left(\frac{Q_{loss} \text{ or } Q_{gain}}{T_o}\right) \tag{7b}$$

In Eq. (7b), the positive and negative signs stand for Q_{loss} and Q_{gain}, respectively.

The thermal storage is necessary under the following two circumstances:

- Heat source is available excessive than the demand, so the excessive energy would be stored.
- Heat source is available but there is no demand, thus, entire energy is to be stored.

In the former case, after the storage, the HTF is used in the application. Therefore, there will be no entropy generation due to the difference between HTF outlet temperature and surrounding temperature (Fig. 3a). On the other hand, the latter case requires discharge of HTF into the atmosphere (Fig. 3b). Due to this, there exits an entropy generation and the same has to be included in the net entropy generation. Thus,

$$S_{gen} = S_{flow} + \Delta S_{PCM} + \Delta S_{HTF} + \Delta S_{wall} \pm \left(\frac{Q_{loss} \text{ or } Q_{gain}}{T_o}\right) + \Delta S_{envn} \tag{7c}$$

The last term on the right hand side of Eq. (7c) denotes the entropy generation due to the discharge of HTF into the atmosphere. In case of discharging process, HTF will always be

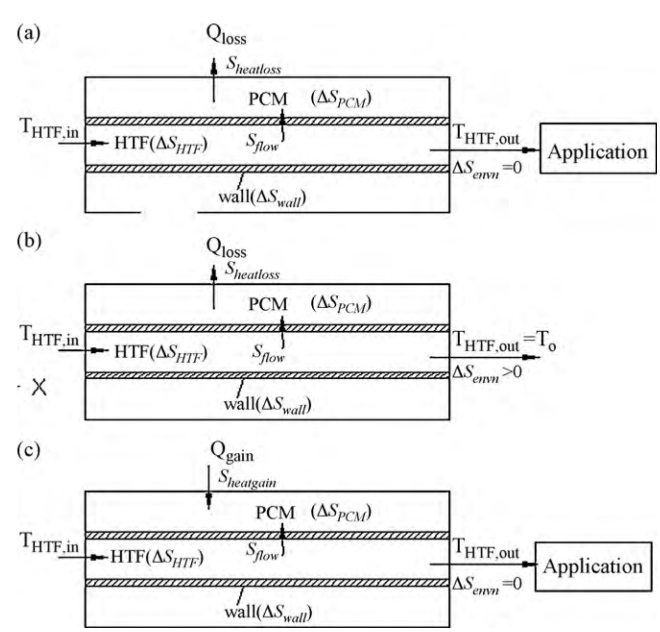

Fig. 3. Entropy generation in a typical LHTS system (a) charging—HTF is used in the application after storage, (b) charging—HTF is dumped into atmosphere and (c) discharging.

used in the application after the energy recovery from the LHTS unit (Fig. 3c). Hence, ΔS_{envn} is always eliminated for discharging.

The terms on the right hand side of Eq. (7c) are given by the following Eqs.

$$S_{flow} = \dot{m}_{HTF} c_{HTF} \int_0^t \ln\left(\frac{T_{HTF,out}}{T_{HTF,in}}\right) dt \tag{8a}$$

Eq. (8a), however, ignores the pressure drop irreversibilities due to the flow of HTF. To include the same, Kousksou et al. [32] have proposed the following expression.

$$S_{flow} = \dot{m}_{HTF} c_{HTF} \int_0^t \ln\left(\frac{T_{HTF,out}}{T_{HTF,in}}\right) dt + \dot{m}_{HTF} R \int_0^t \ln\left(\frac{P_{HTF,in}}{P_{HTF,out}}\right) dt \tag{8b}$$

The second term on the right hand side of Eq. (8b) presents the pressure drop irreversibilities. However, the HTF is assumed to be an ideal gas, which may not be valid in case of liquids. MacPess and Dincer [34] have stated that the entropy generation due to the pressure drop irreversibilities is the entropy generation due to viscous dissipation. Accordingly, Eq. (8b) can be modified as,

$$S_{flow} = \dot{m}_{HTF} c_{HTF} \int_0^t \ln\left(\frac{T_{HTF,out}}{T_{HTF,in}}\right) dt + \frac{\dot{m}_{HTF}\,\Delta t (P_{HTF,in} - P_{HTF,out})}{\rho_{HTF} T_{HTF}} \tag{8c}$$

where T_{HTF} is the average of initial and final temperatures of HTF and the second term on the right hand side of Eq. (8c) is the entropy generation due to the pressure drop irreversibilities.

Now, we address the computation of entropy variation in the PCM. El-Dessouky and Al-Juwayhel [52] have assumed that during the phase change process, the specific Gibbs free energies for solid and liquid phases are same at the melting point. This implies that,

$$h_{PCM,s} - T_m S_{PCM,s} = h_{PCM,l} - T_m S_{PCM,l} \tag{9a}$$

hence,

$$\Delta S_{PCM} = \frac{h_{PCM,s} - h_{PCM,l}}{T_m} = \frac{ML}{T_m} \tag{9b}$$

Eq. (9b) is valid only if the temperature of PCM is equal to its melting point throughout the phase change. For a process in which sensible heat transfer is involved, the expression should take the following form [47].

$$\Delta S_{PCM} = \rho_{PCM,l} L V_{PCM} \int_0^t f(t)\, dt + \rho_{PCM} c_{PCM} V_{PCM} \int_0^t \ln\left(\frac{T_{PCM}(t)}{T_{PCM}(t=0)}\right) dt \tag{9c}$$

The first term on the right hand side of Eq. (9c) denotes the entropy variation in the PCM due to phase change and the second term denotes the entropy variation in the PCM due to sensible heating/cooling.

Similarly, the entropy variation in HTF and wall can be written, respectively,

$$\Delta S_{HTF} = \rho_{HTF} c_{HTF} V_{HTF} \int_0^t \ln\left(\frac{T_{HTF}(t)}{T_{HTF}(t=0)}\right) dt \tag{10}$$

$$\Delta S_{wall} = \rho_{wall} c_{wall} V_{wall} \int_0^t \ln\left(\frac{T_{wall}(t)}{T_{wall}(t=0)}\right) dt \tag{11}$$

The literature review reveals that none of the works considered all the terms appearing in Eq. (7c) together, for the calculation of net entropy generation. This can be seen from Table 5, in which various investigations on evaluation of entropy generation are listed. However, it is recommended that all the terms appearing in the Eq. (7c) need to be considered as each term contributes significantly to the net entropy generation.

Once the entropy generation is known, the destroyed exergy ($Ex_{destroyed}$) can be obtained from the well known *Gousy-Stodala theorem* [35], which is in the following mathematical form,

$$Ex_{destroyed} = T_o S_{gen} \tag{12}$$

Then the exergy efficiency becomes,

$$\psi = 1 - \left[\frac{T_o S_{gen}}{Ex_{in\,put}}\right] \tag{13}$$

As stated earlier, the ratio of destroyed exergy ($T_o S_{gen}$) and exergy input can be replaced by entropy generation number and the expression for exergy efficiency takes the form given in Eq. (1). It is clear from Eq. (1) that the system achieves the maximum efficiency if entropy generation number becomes zero. In other words, the system operates in complete reversible manner and thus, no exergy is destroyed. This ideal condition is possible only if the overall number of transfer units becomes infinite and pressure drop is zero [52]. This highlights the importance of entropy generation number in optimization of the system.

5. Exergy based optimization of LHTS systems

The selection of appropriate values of operating and design parameters is a challenging task as different parameters have different influence on exergy performance of LHTS systems. This section reviews the outcomes of research works reported related to exergy based optimization of operating and design conditions of LHTS systems.

In general, one may expect the performance of LHTS systems is influenced by the following parameters.

- HTF
  - Inlet temperature
  - Mass flow rate/velocity
  - Material

Table 5
Studies on evaluation of entropy generation.

Ref.	LHTS module	Operation mode	Entropy generation terms considered	Pressure drop irreversibility
[32]	Spherical capsules	Charging	S_{flow},ΔS_{PCM}, ΔS_{HTF}	Included
[33]	Spherical capsules	Charging and discharging	S_{flow},ΔS_{PCM}, ΔS_{HTF}, ΔS_{wall}	Included
[45]	Spherical capsules	Charging	S_{flow},ΔS_{PCM}, ΔS_{HTF}	Neglected
[46]	Spherical capsules	Discharging	S_{flow},ΔS_{PCM}, ΔS_{HTF}	Neglected
[47]	Spherical capsules	Charging	S_{flow},ΔS_{PCM}, ΔS_{HTF}	Neglected
[51]	Shell and tube	Discharging	S_{flow},ΔS_{PCM}, ΔS_{HTF}, ΔS_{wall}, $S_{heat\ gain}$	Neglected
[52]	Not available	Cycle	S_{flow},ΔS_{PCM}, ΔS_{HTF},ΔS_{envn}	Included
[55]	Shell and tube	Charging	S_{flow},ΔS_{PCM}, ΔS_{HTF}, ,ΔS_{envn}	Included
[58]	Shell and tube	Cycle	S_{flow},ΔS_{PCM}, ΔS_{HTF}	Included
[77]	Not available	Cycle	S_{flow},ΔS_{PCM}, ΔS_{HTF},ΔS_{envn}	Included

- PCM
  - Melting temperature
  - Initial temperature
  - Material
- System
  - Dimensions
  - Material

5.1. Influence of HTF

The inlet temperature of HTF is very crucial in initiating the charging/discharging process. If the temperature of PCM (initial/melting temperature) is fixed, then there exists a question: what should be the inlet temperature of HTF? The inlet temperature of HTF depends on the heat source during the heat storage and on surroundings during heat recovery. However, it should be controlled for maximizing the exergy performance.

During charging, higher HTF inlet temperature leads to higher temperature difference between HTF and PCM. This would result in higher entropy generation. This is attributed to the fact that the entropy generation is directly proportional to finite temperature difference. This is proved by El-Dessouky and Al-Juwayhel [52] in shell and tube arrangement and more recently by Kousksou et al. [32] in PCM capsules system. Hence, one may conclude that for minimum entropy generation and thus, for maximum exergy performance, the HTF inlet temperature should be as low as possible, i.e. close to the initial temperature of the PCM. However, the smaller temperature difference would effectively affect the heat transfer rate and thus, the charging rate. In LHTS systems employed for applications like waste heat recovery systems, the charging rate should be high, as the source availability is intermittent [53]. Hence, the selection of HTF inlet temperature may be a compromise between the required charging rate and exergy performance. On the other hand, if the LHTS system is employed for solar thermal applications, higher charging rate may not be important. This allows lowest possible HTF inlet temperature and thus, highest exergy efficiency can be realized. At the beginning of discharging process, the PCM in which the energy is already stored would be at a high temperature. From the similar prospective discussed already, the finite temperature difference between PCM and HTF should be reduced in order to decrease the entropy generation and exergy destruction. The results of El-Dessouky and Al-Juwayhel [52] have proved that entropy generation number could be reduced by increasing the HTF (air/water) inlet temperature during discharging, although the effect was marginal when water was used as HTF. This may lead to a conclusion that the effect of HTF inlet temperature on entropy generation is more pronounced when a gas is the HTF than when liquid as HTF. However, this general conclusion is not always valid as Erek and Dincer [51] have shown significant influence of HTF inlet temperature on entropy generation number with ethylene glycol as HTF. Unlike El-Dessouky and Al-Juwayhel [52], Venkataramayya and Ramesh [27] and Erek and Dincer [33] have calculated exergy efficiency based on exergy contents. In both the works carried out with shell and tube module, the authors have found significant increase in exergy efficiency due to increase in HTF inlet temperature during discharging. Like in charging process, operating HTF at a temperature close to PCM temperature is also tricky in discharging process, if higher discharging rate is required.

The exergy performance of LHTS system is also found to be dependent on mass flow rate/velocity of HTF. To study the effect of mass flow rate/velocity of a fluid, the well known dimensionless number called Reynolds (*Re*) number is generally used. Higher *Re* number indicates higher mass flow rate/velocity and vice versa. Recently, Kousksou et al. [47] have reported that the velocity of HTF has almost negligible effect on the entropy generation number. Since the numerical model neglected the entropy generation due to pressure drop in the system, the effects of change in velocity (responsible for pressure drop) on entropy generation number could not be explored. The increase in *Re* number (higher mass flow rate/velocity) obviously results in higher pressure drop and thus, higher entropy generation number. However, the results of Kousksou et al. [32] and Erek and Dincer [51] and have showed the opposite effect. Erek and Dincer [33] have also presented the same results but for exergy efficiency. The reason for this can be given as follows. At higher *Re* numbers, the residing time of HTF in the system becomes less which results in smaller change in the temperature when HTF comes out of the system. Hence, the temperature difference between HTF inlet and outlet decreases as *Re* number increases. Referring to Eqs. (8a) and (8b), it can be stated that the smaller temperature difference would reduce the entropy transfer due to heat transfer between HTF and PCM. Therefore, the net entropy generation can be reduced by increasing *Re* number, although there is an increase in pressure drop irreversibility.

It should be mentioned that none of the above stated works included the pumping power in the exergy analysis. It is evident that high *Re* number requires high pumping power which leads to increase in mechanical irreversibility. Hence, it is also required to take into account the pumping power requirement corresponding to *Re* number, in order to explore the exact influence of *Re* number on entropy generation number. Nevertheless, the influence of *Re* number on exergy performance is reported as less as compared to that of HTF inlet temperature.

5.2. Influence of PCM

The selection of appropriate PCM for any application is also crucial for the proper operation of LHTS systems. In doing so, the melting temperature of PCM is taken as a main criterion although other factors like latent heat, thermal conductivity, stability, availability cost, etc., are taken into consideration. A list of widely studied/potential PCMs of different temperature ranges proposed for different applications can be found in Ref. [54]. For any application, the melting point can be within the operating temperature range of the application. Now the question is what should be optimum melting point within the range? This is where the exergy analysis is of greater help. Kousksou et al. [47] have observed that the irreversibility in the LHTS system is strongly influenced by the melting temperature of PCM.

In general, the optimum melting temperature can be obtained through a simple procedure as explained by Bejan [35]. The operating cycle of LHTS unit consists of heat storage and removal processes, can be assumed to follow Carnot cycle. Accordingly, the heat is supplied at a constant temperature (melting point) and the heat is rejected into a low temperature reservoir (surroundings). This assumption leads to formulation of a reversible cycle executed by the working fluid working between melting temperature and atmospheric temperature. Now, the rate of exergy extracted from the PCM is given as,

$$\dot{E}x = \dot{m}_{HTF} c_{HTF} (T_{HTF,in} - T_m)(1 - e^{-NTU})\left(1 - \frac{T_o}{T_m}\right) \tag{14}$$

Maximizing this exergy with respect to melting temperature leads to,

$$T_m(optimum) = \sqrt{T_{HTF,in} T_o} \tag{15a}$$

Hence, the optimum melting temperature is the geometric mean of HTF inlet temperature and temperature of surroundings. Same condition for optimum melting temperature can be obtained

by minimizing the entropy generation [55] or by maximizing exergy efficiency [40,56]. Although Eq. (15a) has been arrived based on the assumption that PCM is at its melting temperature throughout the cycle, according to Bejan [35] it is still a good approximation even when sensible heat transfer is involved.

Recently, Aghbalou et al. [57] have successfully used Eq. (15a) in their study carried out on LHTS unit consists of PCM filled rectangular slabs. The results showed minimum irreversibility when PCM of optimum melting temperature was used. However, Charach [58] has pointed out that Eq. (15a) is valid only for charging process. As it is known, during the discharging process, the entropy generation would be less if the melting temperature approaches the HTF inlet temperature. Due to this fact, the optimization of melting temperature for the complete cycle (charging and discharging) would result in,

$$T_m(optimum) = \frac{1}{2}(T_{HTF,in} + T_o) \tag{15b}$$

Same expression is also presented by Gong and Mujumdar [40] which was obtained by maximizing the overall exergy efficiency. Charach [58] has also added that the optimum melting temperature is close to arithmetic mean of HTF inlet temperature and temperature of surroundings only for lower HTF inlet temperatures. For higher HTF inlet temperatures, the same was found to be between the arithmetic and geometric means of HTF inlet temperature and temperature of surroundings. On contrary, Conti et al. [59] found two distinct values for optimum melting temperature on the two sides of $(1/2)(T_{HTF,in} + T_o)$ and the lower side value was close to the one found by Charach [58]. Nevertheless, the melting temperature of PCM can be the arithmetic mean of HTF inlet temperature and temperature of surroundings for maximum exergy performance. As already stated, it is more appropriate to focus on complete cycle performance rather than performance during charging or discharging process alone. Hence, it can be mentioned that Eq. (15b) is more appropriate than Eq. (15a).

The selection of appropriate PCM with the required optimum melting temperature is followed by selection of operating condition, i.e. the initial temperature for PCM. The initial temperature of PCM should be in accordance with the inlet temperature of HTF. As explained earlier, the inlet temperature of HTF should be as low as possible for charging and as high as possible for discharging. Hence, it is clear that the initial temperature for PCM should also be low for charging and high for discharging. This means the PCM should be at subcooled and superheated conditions, respectively, at the beginning of charging and discharging processes. Venkataramayya and Ramesh [27] have shown that the overall exergy efficiency of the system with subcooled and superheated PCM is higher than that of system with PCM kept at its melting point. However, the superiority of the former than the latter was found to be established only beyond the optimum melting point. This prompts to conclude that the initial temperature of the PCM may be chosen in accordance with its melting temperature.

5.3. Influence of system dimensions

In any LHTS module, there are generally two compartments separated by a wall which is the heat transfer surface. One compartment is loaded with PCM and HTF flows through the other one. As an example, a typical shell and tube LHTS module showing PCM and HTF compartments is presented in Fig. 4. The volume of the PCM unit is determined by the quantity of PCM to be loaded, which in turn is determined by the quantity of heat to be stored or retrieved. However, for a fixed volume, the dimensions of the unit can still be adjusted to obtain maximum possible exergy performance. The dimensions of the PCM unit are expected to influence the heat transfer mechanism of the phase change process. Since the solidification of PCM is always governed by conduction heat transfer [60], it is generally not affected by the dimensions of the unit. On the other hand, the most part of the melting process is dominated by natural convection in the liquid PCM, although it is initially driven by conduction. The convection dominated melting process is reported by many investigators for almost all configurations. For example, in rectangular module by Stritih [61], in cylindrical module by Regin et al. [6] and in spherical module by Tan [62]. However, Shatikian et al. [63] have shown that the dominance of natural convection is significant only in larger rectangular systems. Similar results are presented by Ettouney et al. [64] for spherical modules. Hence, the increase in vertical dimension of the PCM unit, for instance, the diameter of the shell in case of shell and tube module, promotes the natural convection in the liquid PCM. The increase in natural convection may enhance the heat transfer rate. However, the higher rate of entropy generation is also expected due to faster interface motion and liquid viscosity as a result of enhanced natural convection. Erek and Dincer [33,51] have reported that increasing shell radius reduces the entropy generation number considerably. However, these works are limited to discharging process only. The effect of diameter/height of PCM unit on the overall exergy performance is not reported in the literature so far.

It is understood that decreasing the length and increasing the diameter of the HTF unit could reduce the pressure drop in the HTF flow. This would reduce the entropy generation due to pressure drop irreversibilities. However, decrease in the length of the tube reduces the heat transfer surface area. According to El-Dessouky and Al-Juwayhel [52], entropy generation increases with decrease in heat transfer surface area. In fact, Charach and Zemel [55] have shown that number of transfer (*NTU*) which is a measure of heat transfer surface area (proportional to length) affects the entropy generation in two ways. They are

- The entropy generation due to heat transfer irreversibilities decreases exponentially as the *NTU* increases.

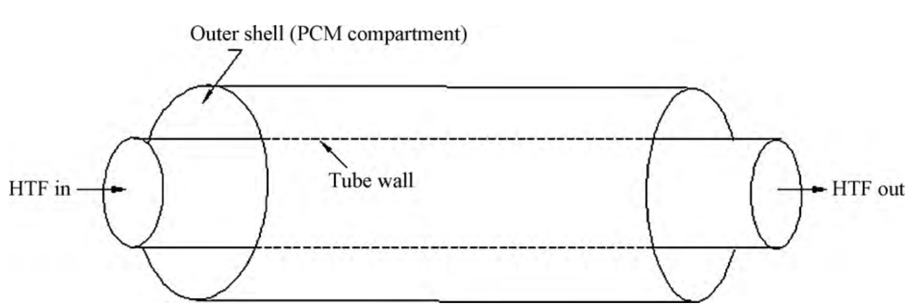

Fig. 4. PCM and HTF compartments in a typical shell and tube LHTS module.

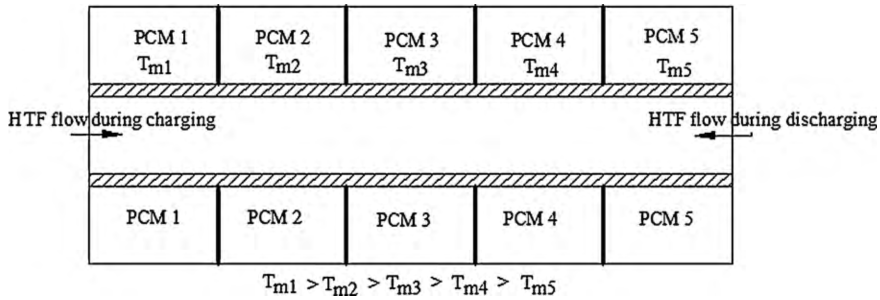

Fig. 5. Arrangement of multiple PCMs in a shell and tube module.

- The entropy generation due to pressure drop irreversibilities increases linearly as the *NTU* increases.

Hence, there exists an optimum value for *NTU*, i.e. heat transfer area or length. This indicates that the length of the tube should be in such way that *NTU* of the unit is optimum.

6. Exergy analysis with performance enhancement techniques

In spite of various advantages like high energy density, nearly isothermal operation, etc., the phase change material loaded in the LHTS unit possesses a very low thermal conductivity, which drastically affects the performance of the unit. The effect of the lower value of conductivity is reflected during energy retrieval or withdrawal with an appreciable temperature drop during the process. As a result, the rate of phase change process (melting/solidification of PCM) has not been up to the expected level and the large scale utilization of LHTS units, remains unsuccessful. Therefore, to tackle the above-mentioned drawbacks, it becomes necessary to improve the thermal performance of the LHTS units employing PCMs. Numerous investigations on various performance enhancement techniques, both numerically and experimentally have been reported so far. The various techniques adopted for enhancing the thermal performance of the LHTS units are enumerated below:

- Using extended surfaces [61,65–68].
- Employing multiple PCMs method [69–72].
- Thermal conductivity enhancement with additives.
- Microencapsulation of PCMs [73–75].

For the recent review on the various performance enhancement techniques employed for LHTS units, readers are referred to the paper by Jegadheeswaran and Pohekar [76].

The studies on LHTS units employing performance enhancement techniques have mainly focused on evaluation of melting/solidification time, heat transfer rate and amount of energy stored/retrieved in comparison with those of system without enhancement techniques. From the results of these studies, it may be stated that all the proposed techniques have good potential in enhancing the thermal performance of LHTS systems. However, the enhancement due to employment of the above listed methods except multiple PCMs method is invariably assessed only through energy analysis. Even for multiple PCMs method, the exergy techniques are employed only by few investigators [38,40,47,77,78].

6.1. Multiple PCMs method

As the name implies, the LHTS system is packed with more than one PCM of different melting temperatures for multiple PCMs method. In case of conventional single PCM system, the temperature of HTF decreases in the direction of flow. As a consequence, the heat transfer rate decreases and thus, leads to poor performance of the unit. If multiple PCMs of different melting temperatures are packed in the unit in the decreasing order of their melting points, then nearly a constant temperature difference can be maintained all along the system, even though the HTF temperature decreases in the flow direction. This leads to almost a constant heat flux to the PCM. During discharging, if the HTF flow direction is reversed then the PCMs remain in the increasing order of their melting points. Once again nearly constant heat flux but from the PCM to HTF is possible. Recently, Bi et al. [79] have noticed that properly controlled uniform phase change rate would result in optimal operating characteristic of LHTS system, i.e. minimum entropy generation. Moreover, poor heat transfer rate from HTF to PCM during charging process results in relatively high temperature HTF at exit. Adebiyi [80] has shown that significant exergy loss would occur, if HTF exits the system at a rather high temperature for a long time during the storage process. This exergy loss can be expected to be less, if multiple PCMs are employed. This is because the HTF temperature at exit would be relatively less in multiple PCMs systems. The employment of multiple PCMs in shell and tube heat exchanger is illustrated in Fig. 5.

The exergy analysis employed for LHTS systems using multiple PCMs may aim at the following:

- To investigate the role of multiple PCMs in improving the exergy performance.
- To identify the number of PCMs required.
- To evaluate the optimum melting point distribution.

As stated above, the use of multiple PCMs is basically for enhancing the charging or discharging rate. Watanabe and Kanzawa [38] have shown that rapid charging or discharging process as a result of multiple PCMs, led to high charging/discharging/overall exergy efficiency under all operating and design conditions. Gong and Mujumdar [40] have found that a maximum of around 100% increase in overall exergy efficiency is possible with three PCMs. It is also reported that the increase can go up to 200% with five PCMs. Domanski and Fellah [77] investigated the improvement in the overall exergy efficiency when using two PCMs. The overall efficiency was calculated using entropy generation number and it was found that the increase was around 40% as compared to single PCM system. Similarly, the overall exergy efficiency of three PCMs system was found to be 74% higher than that of single PCM system by Gong and Mujumdar [78]. This was due to the fact that the charge/discharging process was around 37% faster in three PCMs system. Recently, Kousksou et al. [47] also noticed significant reduction in irreversibility when more number of PCMs were used. Hence, it is clear that multiple PCMs method is very promising from exergy point of view too.

Since the exergy performance increases with increase in number of PCMs, it is also important to identify the number of PCMs that can be used. This important issue is addressed by Gong and Mujumdar [40]. The authors compared the overall exergy

efficiencies of the system using two, three and five PCMs with that of system using single PCM for different *NTU* values. The results revealed that significant improvement in exergy efficiency was obtained, when *NTU* were higher. On the other hand, the increase in exergy efficiency with multiple PCMs was marginal, when *NTU* values were smaller. This indicates that employment of more number of PCMs can be justified only if the heat transfer surface area is more. Hence, it can be stated that the number of PCMs needs to be chosen in accordance with the available heat transfer surface area.

Since the PCMs are having different melting temperatures, attention should also be given to melting temperature distribution. Domanski and Fellah [77] attempted numerically to obtain the melting points corresponding to the best exergy efficiency. However, this study is limited to two PCMs only. It is found that the optimum melting temperature of first PCM increases linearly with inlet temperature of the HTF. As it is known, this is to reduce the entropy generation due to the temperature difference between HTF and PCM. On the other hand, the second PCM (last one) should have a melting temperature close to temperature of atmosphere in order to minimize the amount of exergy loss to the surroundings. Watanabe and Kanzawa [38] have stated that the difference between the highest and lowest melting temperatures has enormous effects on the charging and discharging rates and thus, on the exergy performance. The authors have presented a simple expression for the optimum difference between the highest and lowest melting temperatures as follows.

For charging,

$$T_{m(\text{first PCM})} - T_{m(\text{last PCM})} = \frac{NTU}{1 + (NTU/2)}(T_{HTF,in} - T_{m(ave)}) \tag{16a}$$

where $T_{m(ave)}$ is the average melting temperature of the PCM located at the middle.

For discharging,

$$T_{m(\text{first PCM})} - T_{m(\text{last PCM})} = \frac{NTU}{1 + (NTU/2)}(T_{m(ave)} - T_{HTF,in}) \tag{16b}$$

The two different conditions proposed for charging and discharging are difficult to satisfy as same set of PCMs are generally used for the cyclic operation. Moreover, when more than one PCM is involved, it is also necessary to examine the optimum conditions for melting temperatures of intermediate PCMs. This particular issue is not addressed by Watanabe and Kanzawa [38]. However, Gong and Mujumdar [40] obtained optimum melting temperatures for all PCMs, by maximizing the overall exergy efficiency of multiple PCMs module. The results of case studies based on this procedure indicate that the optimum melting temperatures of PCMs are approximately a geometrical regression i.e. $T_{m1}/T_{m2} \cong T_{m2}/T_{m3} \cong T_{m3}/T_{m4} \cong \ldots\ldots \cong T_{mn-1}/T_{mn}$. Moreover, the ratio between the melting temperatures of two successive PCMs is found to be dependent on *NTU* of the system.

It is clear from the above discussions that only Gong and Mujumdar [40] have investigated the optimum conditions for melting temperatures of all the PCMs in the system. The procedure adopted by the authors seems to be similar to that one used for single PCM system. However, the authors have reported that the maximization of overall efficiency of multiple PCMs system involves complex and tedious mathematical manipulation. The procedure becomes more and more complex as the number of PCMs increases. Hence, guidelines for optimum melting point distribution may not be drawn only based on this procedure. It is felt that comparative studies focusing on different proposals discussed above may lead to a concrete conclusion. It also requires more research as only a limited number of works is reported for exergy analysis of multiple PCMs system. Table 6 summarizes the outcomes of the exergy based investigations on LHTS systems using multiple PCMs.

6.2. Addition of fins, thermal conductivity enhancement and microencapsulation of PCM

Fins are employed for increasing the heat transfer area and thus, heat transfer rate. The conduction governed discharging (solidification) rate can be increased monotonically with increase in number of fins. On the other hand, there exists an optimum number of fins beyond which the convection dominated charging (melting) rate decreases [81]. This is because more number of fins dampens the natural convection in the liquid PCM. Hence, the addition of fins has direct impact on natural convection apart from increasing the heat transfer area (*NTU*). As we have seen, both natural convection in the liquid PCM and *NTU* can significantly affect the entropy generation. Therefore, the optimum number of fins should be computed based on exergy analysis. Since no work is reported on exergy analysis of finned system, it is not yet clear how the addition of fins enhances the exergy performance of LHTS systems.

The conventional PCMs-both organic and inorganic possess very low thermal conductivity ranging from 0.1 to 0.6 W/m K. Hence, the additives of various forms as given below are used to improve the thermal conductivity.

Table 6
Exergy based investigations on LHTS systems using multiple PCMs.

Ref.	Number of PCMs	Operation mode	Approach (Exergy/ Entropy generation)	Operating/design parameters considered	Important findings
[38]	Seven	Charging	Entropy generation	–	Minimum irreversibility when melting temperatures are linear
[40]	Two, three and five	Cycle	Exergy	HTF inlet temperature, *NTU*	Exergy efficiency increases by two to three times with multiple PCMs Optimum melting points of PCMs are approximately a geometric progression
[47]	Fifteen or thirty	Cycle	Exergy	HTF inlet temperature, Initial temperature of PCM	Faster charging or discharging leads to high exergy efficiency Melting point difference between first and last PCM is key for optimum exergy performance
[77]	Two	Cycle	Exergy	Velocity and inlet temperature HTF, *NTU*	Melting temperatures of first and last PCMs to be close to HTF and atmospheric temperatures, respectively, for optimum exergy efficiency
[78]	Three	Cycle	Exergy	Latent heat, *NTU*	Increase in exergy efficiency due to multiple PCMs is not affected by Latent heat of PCM

- High conductivity porous material such as graphite [82–85].
- High conductivity and low density materials such as carbon fibers [86–88].
- High conductivity micro particles such as Aluminium, Copper, Silver, etc., [21,89–91].
- High conductivity metal structures [53,92,93].

In general, however, these additives may lead to loss of storage capacity of pure PCM as the mass of PCM decreases. Therefore, it is important to estimate the optimum mass/volume fraction of additives. It can be stated that the optimization of mass/volume fraction of additives should not be from storage point of view alone. This is because the additives of any form are expected to contribute to the total entropy generation. The same reason can be given for the need of exergy analysis in case of microencapsulation as solid structures are used for encapsulation of PCM.

7. Thermoeconomic analysis

It is important to note that the analyses of different researchers have firmly established the need to employ second law techniques to design thermodynamically efficient thermal energy storage systems. It is well known that, when a component of a thermal storage system displays a deterioration in terms of irreversibility, not only its performance, but also those of the remaining units which make up the system, are affected. In general, this makes difficult to understand what is the effect of a deterioration increase for the overall system, and, consequently, to determine for anyone of the components characterized by irreversibility, how the overall performance of the system would increase, if that irreversibility was eliminated. Thermoeconomics and its application to engineering energy systems can help to answer these questions.

As stated above, thermoeconomic analysis combines economic and thermodynamic analysis by applying the concept of cost (originally an economic property) to exergy (an energetic property) (see Valero and Lozano [94]). Most analysts agree that exergy is the most adequate thermodynamic property to associate with cost since it contains information from the second law of thermodynamics and accounts for energy quality. Exergy based thermoeconomics methods are also referred to as "exergoeconomics".

Thermoeconomic analysis is based on the representation of a thermal system by using a thermoeconomic model. This is done by describing the system by means of a productive structure [95,96]. The productive structure (also "functional diagram" or "structural scheme") is a graph which shows a set of relations defining the interaction among components themselves and the environment. Each subsystem has one or more entering flows that represent the resources or *fuel* and exiting flows (*product*). Due to irreversibilities, in every component, product is smaller than fuel. So, the amount of resources per unit of exergy increases throughout the system. This leads us to the concept of cost.

Many thermal engineers have studied thermoeconomics or exergoeconomics, and various methodologies have been suggested. According to Tsatsaroni [97], thermoeconomics methods can be subdivided into two categories, those based on cost accounting and those based on optimization techniques. Cost accounting methods help to determine actual exergy cost and provide a rational basis for pricing, while optimization methods are used to find the optimum design or operating conditions [98].

The main feature of the thermoeconomics methods is that they propose a cost balance equation applying the exergetic unit cost to the exergy balance equation according to a specific principle [99]. As it was confirmed in related works [100,101], the cost structure of the overall system is mostly affected by the entropy production rate (irreversilbility) at each component and is dependent on the level of aggregation of the system. The level of aggregation provides a breakdown of the total irreversibility among the system components. The chosen level of aggregation will affect the conclusion of the analysis.

In the scope of energy storage systems, to the best of the authors' knowledge very few investigations using thermoeconomics methods have been reported [41,102]. Demirel and Ozturk [41] have performed the cost accounting method to study a seasonal latent storage system for heating a greenhouse. In order to build up the cost formation in the system, structural diagrams have been used. To simplify the cost balance model, all the work interactions for fans, valves and pressure changes in each component are assumed to be negligible. The cost rate balance is established for both charging and discharging modes. They found that the feasibility of overall design and operation of the thermal storage system can be enhanced using the cashflow-diagram based on exergy considerations. Badar et al. [103] and Badar and Zubair [104] discussed the second law-based thermoeconomic analysis of a sensible heat storage system. They described the procedure for optimizing the performance of a thermal energy storage system, which has no removal cycle. They also compared the results with that obtained from Bejan's analysis [23]. Recently, Zubair and Al-Naglah [105] extended thermoeconomic analysis of a storage system that has both energy storage and removal processes with convection by ideal gas. They found that the unit cost of irreversible losses due to heat transfer is relatively more sensitive to the number of units transfer when compared to that of due to pressure drop. To optimize the performance of the studied system they have introduced a new performance criterion described as the cost rate number.

In general, the objective of thermoeconomic optimization is to minimize the annualized total cost of owning and operating the system. The total cost is composed of additive terms that measure the costs associated with the lost exergy and the annualized capital costs of the equipment. However, thermal energy storage (TES)-based systems are usually economically justifiable when the annualized capital and operating costs are less than those costs for primary generating equipment supplying the same service loads and periods. TES is mainly installed to lower the initial costs of the other plant components and operating costs. Lower initial equipment costs are usually obtained when large durations occur between periods of demand. Operating cost savings and the net overall costs should be assessed using life cycle costing or other suitable methods to determine which system is the most beneficial. From this analysis, the aim of thermoeconomic optimization based on exergetic analysis must be directed towards minimizing the exergetic cost of the system. So, the problem of thermoeconomics analysis applied to energy storage systems can be formulated as follows: Given a system whose limits have been defined and a level of aggregation that specifies the components which constitute it, how to obtain the cost of all the flows that become interrelated in this system. This statement is a cornerstone in thermoeconomics. It is also necessary to mention that the results of the thermoeconomic analysis of the energy storage systems will mainly dependent upon:

- the storage period required (i.e., diurnal, weekly or seasonal),
- the defined limits of the system and the definition of resources are always partial and refer to the system under study. Generally speaking, energy, raw materials, PCMs, economy and labour resources are those which are put at the disposal of the system within its limits of analysis and with known unit prices.

8. Conclusions

In the present paper, the various techniques adopted for the exergy based performance evaluation of LHTS units and subse-

quent optimization of the system have been reviewed. This review intends to motivate the researchers to focus more on exergy analysis in the future research works on LHTS systems. To conclude, the following points are highlighted.

- Exergy based performance evaluation of LHTS system can be stated as more perspective measure than energy based one as it reflects the true potential of the system and the economic value of the storage/recovery operation.
- Exergy analysis of any form should consider the complete cycle operation of LHTS systems rather than considering either storage or recovery mode alone.
- Optimization of any LHTS module requires rigorous exergy analysis along with energy analysis.
- Entropy generation analysis has a significant importance especially when it comes to optimization of design and operating parameters of LHTS systems.
- Studies still remain on large scale especially for the comparative evaluation of various performance enhancement techniques employed for LHTS systems.
- The installation and operation of any LHTS system can be justified only if the exergetic cost of the system is minimum and exergy based thermoeconomic optimization is of greater help in minimizing the exergetic cost of the system.

References

[1] Farid MM, Khudhair AM, Razack SAK, Al-Hallaj S. A review on phase change energy storage: materials and applications. Energy Convers Manage 2004;45:1597–615.
[2] Sharma SD, Sagara K. Latent heat storage materials and systems: a review. Int J Green Energy 2005;2:1–56.
[3] Zalba B, Marin JM, Cabeza LF, Mehling H. Review on thermal energy storage with phase change: materials, heat transfer analysis and applications. Appl Therm Eng 2003;23:251–83.
[4] Kenisarin M, Mahkamov K. Solar energy storage using phase change materials. Renew Sustain Energy Rev 2007;11:1913–65.
[5] Trp A. An experimental and numerical investigation of heat transfer during technical grade paraffin melting and solidification in a shell and tube latent heat thermal energy storage unit. Sol Energy 2005;79:648–60.
[6] Regin AF, Solanki SC, Saini JS. Latent heat thermal storage using cylindrical capsule: numerical and experimental investigations. Renew Energy 2006;31:2025–41.
[7] Zukowski M. Mathematical modeling and numerical simulation of a short term thermal energy storage system using phase change material for heating applications. Energy Convers Manage 2007;48:155–65.
[8] Chen CR, Sharma A, Tyagi SK, Buddhi D. Numerical heat transfer studies of PCMs used in a box-type solar cooker. Renew Energy 2008;33:1121–9.
[9] Akgun M, Aydin O, Kaygusuz K. Thermal energy storage performance of paraffin in a novel tube-in-shell system. App Therm Eng 2008;28:405–13.
[10] Guo C, Zhang W. Numerical simulation and parametric study on new type of high temperature latent heat thermal energy storage system. Energy Convers Manage 2008;49:919–27.
[11] Verma P, Varun, Singal SK. Review of mathematical modeling on latent heat thermal energy storage systems using phase-change material. Renew Sustain Energy Rev 2008;12:999–1031.
[12] El Qarnia H. Numerical analysis of a coupled solar collector latent heat storage unit using phase change materials for heating the water. Energy Convers Manage 2009;50:247–54.
[13] Kaygusuz K. Phase change energy storage for solar heating systems. Energy Sources 2003;25:791–807.
[14] Seeniraj RV, Velraj R, Narasimhan NL. Thermal analysis of a finned-tube LHTS module for a solar dynamic power system. Heat Mass Transfer 2002;38:409–17.
[15] Canbazoglu S, Sahinaslan A, Ekmekyapar A, Aksoy YG, Akarsu F. Enhancement of solar thermal energy storage performance using sodium thiosulfate pentahydrate of a conventional solar water-heating system. Energy Buildings 2005;37:235–42.
[16] Gumus M. Reducing cold-start emission from internal combustion engines by means of thermal energy storage system. App Therm Eng 2009;29:652–60.
[17] Devahastin S, Pitakusuriyarat S. Use of latent heat storage to comserve energy during drying and its effect on drying kinetics of a food product. App Therm Eng 2006;26:1705–13.
[18] Mettawee EBS, Assassa GMR. Experimental study of a compact PCM solar collector. Energy 2006;31:2958–68.
[19] Kaizawa A, Kamano H, Kawai A, Jozuka T, Senda T, Maruoka N, et al. Thermal and flow behaviors in heat transportation container using phase change material. Energy Convers Manage 2008;49:698–706.
[20] Mawire A, McPherson M. Experimental characterization of a thermal energy storage system using temperature and power controlled charging. Renew Energy 2008;33:682–93.
[21] Mettawee ES, Assassa GMR. Thermal conductivity enhancement in a latent heat storage system. Sol Energy 2007;81:839–45.
[22] Sharma SD, Iwata T, Kitano H, Sagara K. Thermal performance of a solar cooker based on an evacuated tube solar collector with a PCM storage unit. Sol Energy 2005;78:416–26.
[23] Bejan A. Two thermodynamic optima in the design of sensible heat units for energy storage. J Heat Transfer 1978;100:708–12.
[24] Rosen MA, Pedinelli N, Dincer I. Energy and exergy analyses of cold thermal storage systems. Int J Energy Res 1999;23:1029–38.
[25] Rosen MA. The exergy of stratified thermal energy storages. Sol Energy 2001;71:173–85.
[26] Kaygusuz K, Ayhan T. Exergy analysis of solar-assisted heat-pump systems for domestic heating. Energy 1993;18:1077–85.
[27] Venkataramayya A, Ramesh KN. Exergy analysis of latent heat storage systems with sensible heating and subcooling of PCM. Int J Energy Res 1998;22:411–26.
[28] Sari A, Kaygusuz K. Energy and exergy calculations of latent heat energy storage systems. Energy Sources 2000;22:117–26.
[29] Sari A, Kaygusuz K. First and second laws analyses of a closed latent heat thermal energy storage system. Chinese J Chem Eng 2004;12:290–3.
[30] Ozturk HH. Experimental evaluation of energy and exergy efficiency of a seasonal latent heat storage system for green house heating. Energy Convers Manage 2005;46:1523–42.
[31] Koca A, Oztop HF, Koyun T, Varol Y. Energy and exergy analysis of a latent heat storage system with phase change material for solar collector. Renew Energy 2008;33:567–74.
[32] Kousksou T, El Rhafiki T, Arid A, Schall E, Zeraouli Y. Power, efficiency, and irreversibility of latent energy systems. J Thermophy Heat Transfer 2008;22:234–9.
[33] Erek A, Dincer I. A New approach to energy and exergy analyses of latent heat storage unit. Heat Transfer Eng 2009;30:506–15.
[34] MacPee D, Duncer I. Thermodynamic analysis of freezing and melting processes in a bed of spherical PCM capsules. ASME J Sol Energy Eng 2009;131:031017/1–131017/.
[35] Bejan A. Entropy generation minimization. London (England): CRC press; 1996.
[36] Dincer I, Cengel YA, Energy. entropy and exergy concepts and their roles in thermal engineering. Entropy 2001;3:116–49.
[37] Rosen MA. Appropriate thermodynamic performance measures for closed systems for thermal energy storage. ASME J Sol Energy Eng 1992;114: 100–5.
[38] Watanabe T, Kanzawa A. Second law optimization of a latent heat storage system with PCMs having different melting points. Heat Recovery Syst CHP 1995;15:641–53.
[39] Rosen MA, Dincer I. Exergy methods for assessing and comparing thermal storage systems. Int J Energy Res 2003;27:415–30.
[40] Gong ZX, Mujumdar AS. Thermodyanamic optimization of the thermal process in energy storage using multiple phase change materials. App Therm Eng 1996;17:1067–83.
[41] Demirel Y, Ozturk HH. Thermoeconomics of seasonal latent heat storage systems. Int J Energy Res 2006;30:1001–12.
[42] Krane RJ. A second law analysis of the optimum design and operation of thermal energy storage systems. Int J Heat Mass Transfer 1987;30:43–57.
[43] Bellecci C, Conti M. Phase change energy storage: entropy production, irreversibility, and second law efficiency. Sol Energy 1994;53:163–70.
[44] Farid MM, Kanzawa A. Thermal performance of a heat storage module using PCM's with different melting temperatures: mathematical modeling. ASME J Sol Energy Eng 1989;111:152–7.
[45] Strub F, Bedecarrats JP. Numerical second law analysis of a refrigeration phase-change storage. Int J Thermodynamics 1999;2:133–8.
[46] Strub F, Bedecarrats JP. Thermodynamics of phase-change energy storage: the effects of undercooling on entropy generation during solidification. Int J Thermodynamics 2000;3:35–42.
[47] Kousksou T, Strub F, Lasvignottes JS, Jamil A, Bedecarrats JP. Second law analysis of latent thermal storage for solar system. Sol Energy Mater Sol Cells 2007;91:1275–81.
[48] Sharma A, Tyagi VV, Chen CR, Buddhi D. Review on thermal energy storage with phase change materials and applications. Renew Sustain Energy Rev 2009;13:318–45.
[49] Lacroix M. Study of the heat transfer behavior of a latent heat thermal energy storage unit with a finned tube. Int J Heat Mass Transfer 1993; 36:2083–92.
[50] Jegadheeswaran S, Pohekar SD. Numerical investigations on the performance enhancement of a latent heat thermal storage unit with particle laden phase change material. In: Proceedings of 6th International Conference on Computational Heat and Mass Transfer; 2009.
[51] Erek A, Dincer I. An approach to entropy analysis of a latent heat storage module. Int J Therm Sci 2008;47:1077–85.
[52] El-Dessouky H, Al-Juwayhel F. Effectiveness of a thermal energy storage system using phase-change materials. Energy Convers Manage 1997; 38:601–17.
[53] Velraj R, Seeniraj RV, Hafner B, Faber C, Schwarzer K. Heat transfer enhancement in a latent heat storage system. Sol Energy 1999;65:171–80.

[54] Agyenim F, Hewitt N, Eames P, Smyth M. A review of materials and phase change problem formulation for latent heat thermal energy storage systems (LHTESS). Renew Sustain Energy Rev 2010;14:615–28.
[55] Charach Ch, Zemel A. Thermodynamic analysis of latent heat storage in a shell-and-tube heat exchanger. ASME J Sol Energy Eng 1992;114:93–9.
[56] Bjustrom H, Carlsson B. An exergy analysis of sensible and latent heat storage. Heat Recovery Syst CHP 1985;5:233–50.
[57] Aghbalou F, Badia F, Illa J. Exergetic optimization of solar collector and thermal energy storage system. Int J Heat Mass Transfer 2006;49:1255–63.
[58] Charach Ch. Second-law efficiency of an energy storage-removal cycle in a phase-change material shell-and-tube heat exchanger. ASME J Sol Energy Eng 1993;115:240–3.
[59] Conti M, Bellecci C, Charach Ch. Thermodynamic design of a phase change thermal storage module. ASME J Sol Energy Eng 1996;118:89–96.
[60] Ettouney H, El-Dessouky H, Al-Kandari E. Heat transfer characteristics during melting and solidification of phase change energy storage process. Ind Eng Chem Res 2004;43:5350–7.
[61] Stritih U. An experimental study of enhanced heat transfer in rectangular PCM storage. Int J Heat Mass Transfer 2004;47:2841–7.
[62] Tan FL. Constrained and unconstrained melting inside a sphere. Int Commun Heat Mass Transfer 2008;35:466–75.
[63] Shatikian V, Ziskind G, Letan R. Numerical investigation of a PCM-based heat sink with internal fins. Int J Heat Mass Transfer 2005;48:3689–706.
[64] Ettouney H, El-Dessouky H, Al-Ali A. Heat transfer during phase change of paraffin wax stored in spherical shells. ASME J Sol Energy Eng 2005;127: 357–65.
[65] Lamberg P. Mathematical modeling and experimental investigation of melting and solidification in a finned phase change material storage. Doctoral Dissertation, Department of Mechanical Engineering, Helsinki University of Technology, Espoo, Finland, 2003.
[66] Lamberg P, Lehtiniemi R, Henell AM. Numerical and experimental investigation of melting and freezing processes in phase change material storage. Int J Therm Sci 2004;43:277–87.
[67] Reddy KS. Thermal modeling of PCM-based solar integrated collector storage water heating system. ASME J Sol Energy Eng 2007;129:458–64.
[68] Gharebaghi M, Sezai I. Enhancement of heat transfer in latent heat storage modules with internal fins. Numer Heat Transfer Part A 2008;53: 749–65.
[69] Cui H, Yuan X, Hou X. Thermal performance analysis for a heat receiver using multiple phase change materials. Appl Therm Eng 2003;23:2353–61.
[70] Fang M, Chen G. Effects of different multiple PCMs on the performance of a latent thermal energy storage system. Appl Therm Eng 2007;27:994–1000.
[71] Seeniraj RV, Narasimhan NL. Performance enhancement of a solar dynamic LHTS module having both fins and multiple PCMs. Sol Energy 2008;82: 535–42.
[72] Adine HA, El-Qarnia H. Numerical analysis of the thermal behavior of a shell-and-tube heat storage unit using phase change materials. Appl Math Modell 2009;33:2132–44.
[73] Hawlader MNA, Uddin MS, Zhu HJ. Encapsulated phase change materials for thermal energy storage: experiments and simulation. Int J Energy Res 2002;26:159–71.
[74] Smith MC, Farid MM, Easteal AJ. Microencapsulated phase change materials for thermal energy storage applications. In: Proceedings of IIR/IRHACE Conference; 2006.
[75] Ozonur Y, Mazman M, Paksoy HO, Evliya H. Microencapsulation of coco fatty acid mixture for thermal energy storage with phase change material. Int J Energy Res 2006;30:741–9.
[76] Jegadheeswaran S, Pohekar SD. Performance enhancement in latent heat thermal storage system: a review. Renew Sust Energy Rev 2009; 13:2225–44.
[77] Domanski R, Fellah G. Exergy analysis for the evaluation of a thermal storage system employing PCMs with different melting temperatures. Appl Therm Eng 1996;16:907–19.
[78] Gong ZX, Mujumdar AS. Finite element analysis of a multistage latent heat thermal storage system. Numer Heat Transfer Part A 1996;30:669–84.
[79] Bi Y, Guo T, Zhang L, Chen L, Sun F. Entropy generation minimization for charging and discharging processes in a gas-hydrate cool storage system. Appl Energy 2010;87:1149–57.
[80] Adebiyi GA. A Second-law study on packed bed energy storage systems utilizing phase-change materials. ASME J Sol Energy Eng 1991;113:146–56.
[81] Lacroix M, Benmadda M. Analysis of natural convection melting from a heated wall with vertically oriented fins. Int J Numer Methods Heat Fluid Flow 1998;8:465–78.
[82] Sari A, Karaipekli A. Thermal conductivity and latent heat thermal energy storage characteristics of paraffin/expanded graphite composite as phase change material. Appl Therm Eng 2007;27:1271–7.
[83] Pincemin S, Olives R, Py X, Christ M. Highly conductive composites made of phase change materials and graphite for thermal storage. Sol Energy Mater Sol Cells 2008;92:603–13.
[84] Pincemin S, Py X, Olives R, Christ M, Oettinger O. Elaboration of conductive thermal storage composites made of phase change materials and graphite for solar power plant. ASME J Sol Energy Eng 2008;130:11005–9.
[85] Kim S, Drzal LT. High latent heat storage and high thermal conductive phase change materials using exfoliated graphite nanoplatelets. Sol Energy Mater Sol Cells 2009;93:136–42.
[86] Fugai J, Hamada Y, Morozumi Y, Miyatake O. Improvement of thermal characteristics of latent heat thermal energy storage units using carbon-fiber brushes: experiments and modeling. Int J Mass Heat Transfer 2003;46: 4513–25.
[87] Hamada Y, Ohtsu W, Fugai J. Thermal response in thermal energy storage material around heat transfer tubes: effect of additives on heat transfer rates. Sol Energy 2003;75:317–28.
[88] Nakaso K, Teshima H, Yoshimura A, Nogami S, Hamada Y, Fugai J. Extension of heat transfer area using carbon fiber cloths in latent heat thermal energy storage tanks. Chem Eng Process 2008;47:879–85.
[89] Seeniraj RV, Velraj R, Narasimhan NL. Heat transfer enhancement study of a LHTS unit containing dispersed high conductivity particles. ASME J Sol Energy Eng 2002;124:243–9.
[90] Khodadadi JM, Hosseinizadeh SF. Nanoparticle-enhanced phase change materials (NEPCM) with great potential for improved thermal energy storage. Int Commun Heat Mass Transfer 2007;34:534–43.
[91] Zeng JL, Sun LX, Xu F, Tan ZC, Zhang ZH, Zhang J, et al. Study of a PCM based energy storage system containing Ag nanoparticles. J Therm Analys Calorimetry 2007;87:369–73.
[92] Ettouney H, Alatiqi I, Al-Sahali M, Al-Ali SA. Heat transfer enhancement by metal screens and metal spheres in phase change energy storage systems. Renew Energy 2004;29:841–60.
[93] Ettouney H, Alatiqi I, Al-Sahali M, Al-Hajirie K. Heat transfer enhancement in energy storage in spherical capsules filled with paraffin wax and beads. Energy Convers Manage 2006;47:211–28.
[94] Valero A, Lozano MA. An introduction of thermoeconomics. In: Boehm RF, editor. Developments in the design of thermal systems. Cambridge (United Kingdom): Cambridge University Press; 2005. p. 203–23.
[95] Lozano ML, Valero A, Serra L. Local optimization of energy systems. Atlanta (USA): Proceeding of the ASME Advanced Energy Systems Division 1996; 36:241–50.
[96] Frangopoulos CA. Thermoeconomic functional and optimization. Energy 1987;19:563–71.
[97] Tsatsaroni G. A review of exergoeconomic methodologies. In: Moran MJ, Sciubba E, editors. Second law analysis of thermal systems. New York (USA): ASME Book I00236; 1987. p. 81–7.
[98] Abusoglu A, Kanoglu M. Exergoeconomic analysis and optimization of combined heat and power production: a review. Renew Sust Energy Rev 2009;13:2295–308.
[99] Kim DJ. A new thermoeconomic methodology for energy systems. Energy 2010;35:410–22.
[100] Lozano MA, Valero A. Theory of the exergetic cost. Energy 1993;18:939–60.
[101] Erlach B, Serra L, Valero A. Structural theory as standard for thermoeconomics. Energy Convers Manage 1999;40:1627–49.
[102] Demirel Y. Heat storage by phase changing materials and thermoeconomics. In: Paksoy HO, editor. Thermal energy storage for sustainable energy consumption. Dordrecht (Netherlands): Springer; 2007. p. 133–51.
[103] Badar MA, Zubair SM, Al-Farayedhi. Second-law-based thermoeconomic optimization of a sensible heat thermal energy storage system. Energy Int J 1993;18:641–9.
[104] Badar MA, Zubair SM. On thermoeconomic of a sensible heat thermal energy storage system. ASME J Sol Energy Eng 1995;117:225–59.
[105] Zubair SM, Al-Naglah MA. Thermoeconomic optimization of a sensible heat thermal storage system: a complete cycle. ASME J Energy Res Tech 1999;121:286–94.